THE PURIFICATION OF CARBON RODS FOR SPECTROGRAPHIC ANALYSIS BY CATHODE LAYER ARC

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(Plate III)

ABSTRACT Different methods of purification of carbon rods which can be used as electrodes in the carbon arc cathode layer method of spectrographic analysis have been studied and suitable conditions for purification have been worked out by combinations of both chemical and thermal methods and by the method of resistance heating as employed by Gatterer. The degree of purification of the carbon rods has always been studied in the E_1 spectrograph with Twyman-Simeon lens arrangement by the cathode layer method with an arc current of 11 amp. at 220 volts, D C.

INTRODUCTION

In the carbon arc cathode layer method of spectrographic analysis developed by Maunkopff and Peters (1931) carbon electrodes of very high purity must have to be used. The line spectra of most elements in the cathode layer are 10 to 100 times stronger than in the main arc gas column (Strock, 1936). Spectrum lines of the impurities in concentrations down to 0.0001% (a concentration of 0.0001% in 1 mg. is 10^{-9} gm.) present are clearly recorded in the cathode layer photograph. Lines of the impurities below this amount also distinctly appear in the region adjoining the cathode. These requirements are not satisfied by the methods of purification generally followed.

The methods of purification developed so far can be classified broadly under two heads, *viz.* (1) method of chemical treatment followed by heat treatment and (2) method of resistance heating under heavy current. Early investigators first tried to purify carbon rods by subjecting them to heat treatment either in vacuum or in atmospheres of certain gases, and later, chemical treatment was combined with heat treatment.

Moissan obtained graphite from impure carbon rods by the method of electric arc treatment and observed that the graphite so obtained was purer the higher the temperature in the arc. Lebeau and Picon (1924) started with graphite containing 0.1 to 0.2% ash and after heating it for three hours in vacuum at 2000°C obtained graphite containing only 0.005% to 0 006% ash. They further observed that graphite containing sulphurous matters could not be purified by heating it even at 2200°C, and impurities amounting to 0.185% persisted after this heat treatment. Heyne (1930) tried to purify carbon rods by heating them in an electric tube furnace at 2500°C-3000°C in atmospheres of air, nitrogen and hydrogen. He observed that even at 3000°C Ca, Mg,

Ti, V and above all B were not eliminated completely. He also found that the rods heated at 2000°C for 15 minutes in an atmosphere of Cl_2 were superior to those heated at 3000°C in the atmosphere of N_2 and H_2. Zurer and Treadwell (1935) purified parts of carbon electrodes by arcing in an atmosphere of nitrogen or argon containing 5% chlorine. The best purification was obtained by arcing for 3 minutes, but ultimate lines of Mg, Ca, Co and B were found to be present in the spectrum of the arc formed between carbon rods thus purified. Standen and Kovach (1935) worked out two methods for the elimination of impurities except Si and B. The chemical treatments followed in the second method were found to be satisfactory and were developed in the present investigation. Next Staud (1938) tried to purify carbon rods by first treating them in acids and then heating in oxy-gas burner He tried to remove Si by treating the carbon rods in hydrofluoric acid but the method proved a failure. Pierce, Torres and Marshall (1940) tried to purify Acheson graphite rods by refluxing them first in nitric and hydrochloric acids and then in 6M hydrochloric acid. Graphite thus purified contained B, Si, Cu, Ca, Mg and Na. The amount of Cu, Na, Mg and Ca was, however, reduced greatly on arcing the rods at 10 amps for 1 minute. The spectrographic examination of the purified carbon rods was not carried out so far by the sensitive cathode layer method.

As regards the second method, *viz.*, that of resistance heating, Russanow (1934) first observed that by resistance heating the purification began at 2250°C and when the temperature went up to even 2000°C traces of Ca, Mg and B persisted, allowing the maximum time of heating to be 3 minutes. Preuss (1935) developed the method of passing currents of 180A-200A through carbon rods 35 cm. in length and 5 mm. in diameter placed in vertical position. Traces of impurities of Ca, Mg, Ti, Al, Fe, Si, B and Ba were still found to be present. Gatterer (1941) passed currents of 300-320A maximum at 70 volts for 30-60 seconds through carbon rods 14 cm. in length and 6 mm. in diameter, held between graphite blocks by a spring arrangement to allow free expansion. For uniform heating a weak current of air was blown during heating. The maximum temperature attained was about 3000°C but still traces of B, Cu, Mg, Ca, Ti and V were present in the purified product, Hoogland (1946) passed still higher current *e.g.*, 400-650A maximum at 30-60 V for 15-60 seconds through carbon rods held horizontally with proper arrangement for free expansion. The main advantage of the horizontal position of the carbon rod was that in the direction of the length the rod not being irregularly heated, the extra cooling by the current of air as used by Gatterer was avoided. The main disadvantage during heating was that the long carbon rod (200 mm. in length, 7 mm. in diameter) which became soft at high temperature attained sagged a little. Starting with "Siemens-Planla Superbio Negative Homogen Kohle" carbon the best product was obtained with a maximum current of 650A passed for 60 secs. The purified carbon rods were analysed in the Hilger-Fully spectrograph by the

cathode layer method with a current of 5.5A and a separation between the electrodes of 5 mm. in the region 2450A°-3000A and his results of analysis are given in Table 2. Trombe, Foex and Bardet (1945) obtained carbon rods of very high purity by the method of resistance heating with a current of 600A maximum (temperature maximum 2050°C) passed through carbon rods (length 300 mm. diameter 8 mm.) for 5 minutes in the atmosphere of nitrogen, hydrogen and also air in a specially constructed chamber. But the method of analysis of the purified carbon rods was not the sensitive cathode layer method. The light of the arc was photographed in the Hilger large dispersion quartz spectrograph for 1 min., the arc functioning between carbon electrodes placed horizontally at 12 amps., 40 volts.

The object of the present investigation was to make an attempt to develop a method combining chemical treatment with heat treatment for the purification of carbon rods and to examine its purity by the cathode layer method. It was further intended to investigate under what conditions the method of resistance heating give the best results.

EXPERIMENTAL

(A) *Chemical method combined with heat treatment*

In the present investigation "Kino-Homogen" (Germany) carbon rods were used as the starting material. The spectrum of the impurities in a heavily exposed cathode layer photograph in the region 2500A°-3500A° of the carbon electrodes under a current of 11 amps. at 220 V revealed the presence of the following impurities: Fe, B, Si, Cu, Ni, Ti, Al, Mg, Na, Ca, Mn in large amounts and Ag, V, Zn, Bi, Cd, Sn, Ga, Pb, Cr, As, K and Co in small traces. (See Plate III).

The carbon rods were each 20 cm. in length and 7 mm. in diameter. Each was cut into three pieces and 100 such pieces were boiled in 1 : 1 mixture of concentrated HCl and HNO_3 for 5 hours in a flask, fitted with a reflux condenser. The acids were then replaced by fresh quantity and boiled for 4 hours. The flask was placed over a lamp at 80°C for 12 hours and subsequently washed by decantation with distilled water. These carbon rods were next boiled in pure conc. H_2SO_4 for 3 hours and placed over the lamp at 80°C for 12 hours. The process of washing with distilled water was repeated. Then they were boiled for 1 hour in liquor ammonia and placed over the lamp at 60°C for 12 hours. Subsequently the rods were washed with distilled water, then boiled in glacial acetic acid for 3 hours and placed over the lamp at 80°C for 12 hours. The carbon rods were washed with distilled water, boiled in it for 2 hours and again washed by decantation. Then they were heated to boiling pt. in liquor ammonia and again washed with distilled water. Finally the carbon rods were dried in an electrical furnace at 100°C. After each heat treatment the rods were allowed to cool before the next operation. The whole chemical process and specially the glacial

acetic acid and pure conc. H_2SO_4 treatment was very effective for the preliminary purification.

The principle of the next thermal treatment was to remove the easily volatile compounds in the chemically treated carbon rods by high temperature heat treatment. Some of the carbon rods were next placed on a silica dish which was heated to redness in oxy-acetylene flame for 30 seconds. The flame was then allowed to play on the rods from all sides for 30 seconds. The carbon rods first gave out black smoke and then became red hot. The temperature as measured by an optical pyrometer was between 1800°C-2000°C. Sometimes it was still higher. The rods when cooled were found to be used up with a surface layer of small black globules.

A simple arrangement for heating these carbon rods again at high temperature in a current of nitrogen bubbled through carbon tetrachloride was made. A Pyrex glass tube with a large bulb at the centre was used as the heating chamber. Two copper rods with arrangements in each for holding a carbon rod horizontally at one end and for electrical connections at the other were used as electrode holders. The copper rods were fitted within two Pyrex glass tubes, each having one side tube for outside connections. These glass tubes, were fitted within the central glass tube using bored corks as sockets. All the leak points were sealed with plasticin and pecien. The heating chamber was evacuated by a Cenco pump connected to a side tube. Nitrogen from the cylinder was bubbled through CCl_4 and then introduced into the heating chamber through the other side tube. Two carbon rods were taken out from the silica dish and clamped into the holders horizontally within the heating chamber. They were burned as electrodes in the arc with 15 amps current for 2 minutes. The arc gap which could be adjusted from outer arrangements was kept small in order to have the temperature through a greater length (1.5 cm.) of the rods near the arc points very high. The chamber was evacuated by the Cenco pump and a continuous current of N_2-gas bubbled through CCl_4 was passed through it. Due to the high temperature near the arc the concentration of the gas at that region was high. The temperature in the carbon electrodes was found to fall abruptly at a distance of nearly 1.5 cm. from the arc gap.

The heating process in the electric arc was carried out in different conditions: (*a*) at 15 A. in air for 2 mins., (*b*) at 15 A. in vacuum for 2 mins., (*c*) at 15 A. in the current of N_2 bubbled through CCl_4 for 2 mins. In each of these conditions part of the carbon rods (about 1.5 cm. at the ends) of high purity were obtained. The best products were obtained in the current of N_2 bubbled through CCl_4. Due to the heat treatment for one minute in oxy-acetylene flame the diameter of the carbon rod was reduced from 7 mm. to 5.5 mm. and the surface layers were found to be in a very porous condition. The heat treatment in oxy-acetylene flame (temperature nearly 2000°C) reduced the impurities throughout the carbon rods and in two minutes arcing the impurities from the part of the carbon rods were greatly reduced.

PLATE III

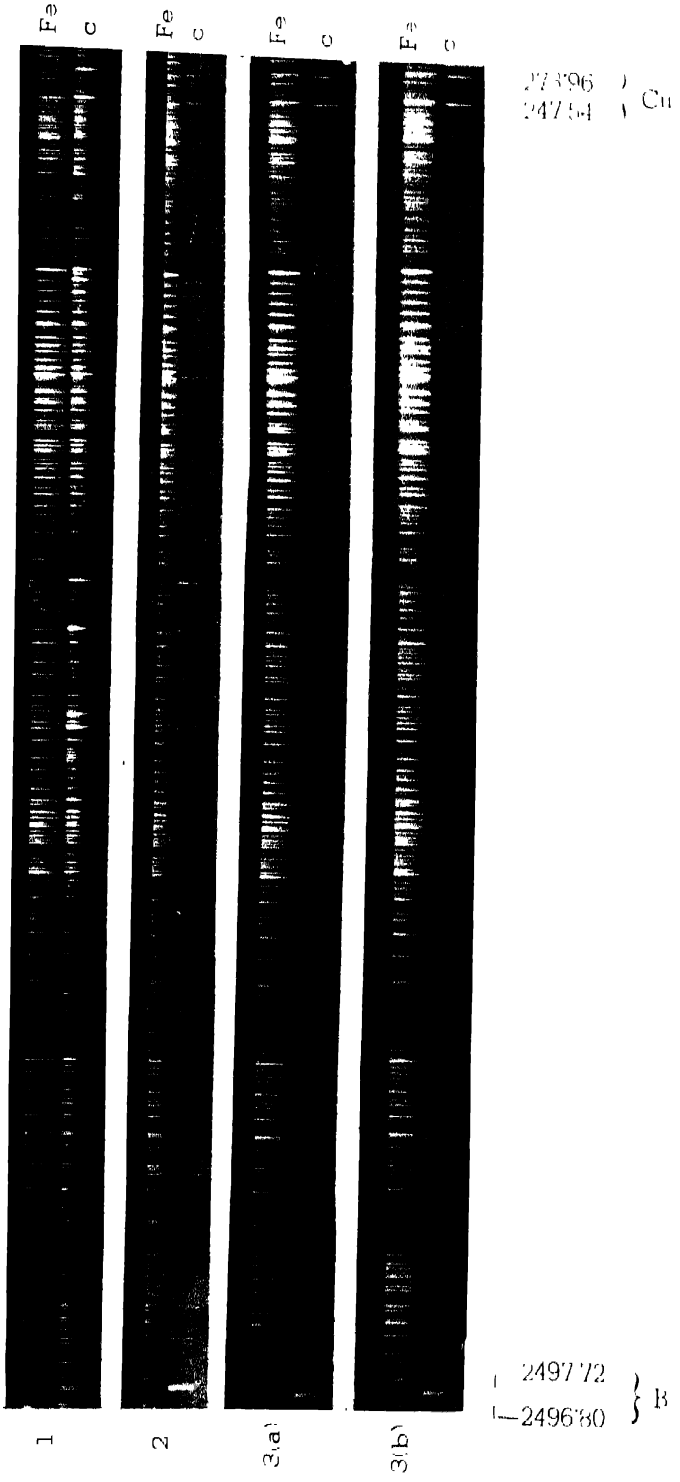

TABLE I

Results of analysis of the purified carbon rods by the cathode layer method (Plate III, 2). Arc current 11 A at 220 v.(d.c.)

Element	Sensitive line * λ in I. Å°	Intensity	Present
B	2497. 72 2496. 80	++	Almost entire amount
Si	2516. 12 2881. 59	+	Considerable traces
Mg	2795. 54 2802. 71 2852. 12	→o	Faint traces
Mn	2794. 82 2798. 27 2801. 08	o	None
Ti	3088. 03 3371. 45 3354. 63	→o←	None to faint traces
Al	3082. 16 3092. 71	→0	Faint traces
Ca	3158. 88 3179 31	→o←	None to faint traces
Cu	3247. 54 3273 96	(+)	Traces
Na	3302. 34 3302- 94	o	None
V	3183. 42 3183. 96	o	None
Fe	3020. 64 3021. 07	(+)	Small traces

(* Wave lengths of the elements according to the table of H. Kayser and R. Ritschl.)

++ = strong line; + = medium line; (+) = faint line;

→o = extremely faint line, a faint point at the base with a faint prolongation.

→o← = None to faint point at the base of the cathode layer; o = undetectable.

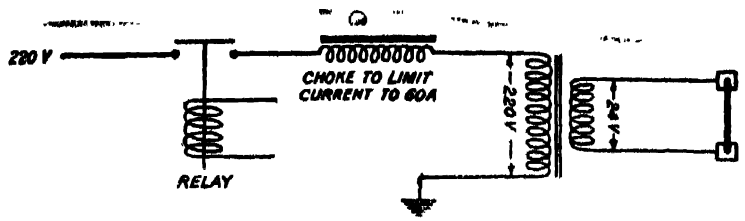

FIG. 1

The final products were analysed by the cathode layer method using a Hilger E_1 quartz spectrograph of very suitable dispersion. An electric supply

of up to 15A. at 220 V. (D.C.) together with tapped resistance and an ammeter to control the current through the arc was used. In order to produce an image of the cathode layer effect on the spectrographic plate the lens arrangement of Twyman and Simeon (1929) was found very satisfactory. The arc was focussed sharply with a quartz condensing lens (F. 27S, Adam Hilger) over a screen in which there was an adjustable circular diaphragm. The diaphragm was adjusted so that it allowed to pass only the edge of the cathode (negative crater) and the overlying arc column, *i.e.*, an opening of about 4 5 mm. The light image of the illuminated opening was again focussed and enlarged by another spherical quartz condensing lens (F. 17, Adam Hilger) on the slit of the spectrograph. During an exposure the arc gap was best controlled by means of an enlarged image thrown at right angles to the former arrangement over a graduated screen by another condensing lens. The cathode image was held just on the edge of the circular aperture and any slight lack of alignment was adjusted by the position of the image of both cathode and anode on the graduated screen. For the purpose of analysis the arc of the purified carbon rods was drawn at 11A, separation between electrodes being 8 mm. With the spectrum of the purified carbon an iron spectrum was taken below which served as a reference wavelength scale. The spectrum photograph was studied under a "Comparator" for the identity of all the lines in the carbon spectrum with the help of "Atlas De Spectres D'Arc" of J. Bardet.

All other impurities originally present in the starting material were absent in the final product. As the method of analysis of the previous investigators was not the same the results were not compared.

B. Method of Resistance Heating.

Gatterer's method in a slightly modified form was employed in the present investigation for purifying carbon rods by resistance heating. It was not possible to copy the apparatus used by Gatterer and Hoogland in this laboratory. Figure 1 shows the arrangement used for resistance heating. The type of holder used though very simple was found to be inconvenient for higher currents.

Two copper blocks were drilled in the middle in order to make a hole whose diameter was slightly less than that of the carbon rod. Both of the blocks were cut into two halves through the centres of the holes. On each block the two halves could be screwed tightly in order to clamp the end of the carbon rod into the hole. On one side of each block, there was an arrangement for connection to the lids of the secondary terminals of the transformer. There was no extra spring arrangement for free expansion and contraction during the process of heating. The blocks were light and could slide freely over a smooth plain surface of mica sheet. Chemically treated carbon rod (by the method given before) of 95 mm. length, 7 mm. in diameter was clamped horizontally on both ends into the holes

of the blocks. At both the ends only 5 mm. of the carbon rod was introduced into the holes. The carbon rod was heated by allowing the current of 550 amps. maximum to pass through the rod from the transformer, the current being limited by a choke in the circuit (primary voltage 220 V. secondary voltage 24 V). The contacts between the rod and the blocks and the electrical connections to the blocks were sufficiently good enough to minimise the high transition resistances.

As the relay was started, during the first 5 secs only black vapour came out from the surface of the carbon rod. Suddenly the rod began to glow, the temperature being nearly 1200°C. The brightness of the glow increased very rapidly and the temperature went up to 1800°C within 10 secs. At about 30 secs. the glow was very intense when the temperature went higher than the maximum temperature range of the optical pyrometer used (*i.e.*, higher than 2000°C) and carbon flames (named by Gatterer) appeared in the bright glow. Suddenly at about 50 secs. the circuit was broken with the formation of an arc at one end. The metal block was found to be melted at the end. The copper blocks must have to be replaced by graphite blocks or there should be an arrangement for cooling the blocks during heat treatment.

This resistance heated carbon rod when cooled, was found to be covered on the surface with loose black globules. Probably due to oxidation the surfaces were used up, which could be avoided, as found in the method (A) if the heating by the passage of current was carried out in the current of nitrogen bubbled through CCl_4. The lengths of the carbon rod used being small, the sag (as found by Hoogland) due to high temperature attained during heating was small.

The resistance heated carbon rod was cut into two equal halves and then used as electrodes in a current of 11A at 220 V with a separation of 8 mm. between them. The light of the cathode layer arc was then analysed in the spectrograph with the lens arrangement as before. During an exposure when the negative crater (cathode) was adjusted just below the edge of the circular diaphragm ultimate lines of Fe and Si were recorded as faint dots at the origin of the cathode layer. But when the cathode was placed just touching the edge of the diaphragm these faint dots were not present at all (Plate 3a and 3b). Thus the faint traces of Fe and Si present were undetectable. By visual inspection under the comparator the percentage of B in this carbon was found to be slightly less than that present in the carbon purified by the previous method, but the percentage of Cu present was greater. During analysis the time of exposure was always 60 secs. the current was 11 A and the separation between the carbon electrodes was 8 mm. Ilford (H. & D. 100) plates and metol hydroquinone developer were always used, the times of development and fixation were 2.5 minutes and 10 minutes respectively at 18°C. Due to a consistent operating technique, the same rocking arrangements during development and the use of fresh developing solution for each plate, spectrum plates of almost identical character were obtained.

In the purification by this method of resistance heating it was found that the carbon rods with preliminary chemical treatment were better purified (as given in Table 2) than the rods without any chemical treatment.

TABLE II

Results of analysis of the purified carbon rods (resistance heated for 50 secs. with i_{max} = 550A). Arc current 11 A.

Element	Sensitive line λ in I.A°	Intensity	Hoogland's results I_{max} = 650 A. Arc current 5.5 A. Time of heating 60 secs.
B	2497. 72 2496. 80	++	++
Si	2516. 12 2881. 59	→o←	?
Mg	2795. 54 2802. 71 2852. 12	→o	+
Mn	2794. 82 2798. 27 2801 08	o	
Ti	3088. 03 3371. 45 3354. 03	→o	?
Al	3082. 16 3092. 71	→o	?
Ca	3158. 88 3179. 34	→o←	(+)
Cu	3247. 54 3273. 96	+	?
Na	3302. 34 3302. 94	o	
V	3183. 42 3183. 96	o	–
Fe	3020. 64 3021. 07	→o	+

Symbols in column 3 are explained as :

++ = almost entire amount ; + = considerable traces ;

o = absent ; →o = faint traces ;

→o← = none to faint traces.

According to Hoogland the symbols in column 4 are given as :

+ = present ; ? = presence uncertain ;

– = absent ; (+) = just barely observable.

In the analysis of the purified carbon rods by the cathode layer method while Hoogland (1946) used a current of 5.5 amps. the author used 11 amps. current, because the spectrographic analysis is usually carried out at 9 to 11 amps. current.

DISCUSSION

The method of chemical treatment conjugated with heat treatment tried in the present investigation in oxy-acetylene flame and in 15 amps. arc in the atmosphere of N_2-Cl_2 mixt. is recommended for the purification of carbon rods in a laboratory. The presence of N_2 and Cl_2 gives more volatile compounds than the oxides. Boron usually forms very non-volatile compounds. As to the properties of the purified carbon rods, they can easily be made into proper shape with new high speed steel machine tools and give steady arc without much flickering, when used as supporting electrodes for spectrographic analysis.

As regards the method of resistance heating, better purification is expected with higher currents passed through the carbon rod for longer times (3 mins. or more) in the atmosphere of N_2 and Cl_2. Deinum (1946) found that $i_{max} = 650$ A was the limiting value up to which the carbon rod (20 cm. length, diameter 7 mm.) could be heated and that the axial temperature attained must be of the order of 3500°C. Hoogland (1946) found that all carbon rods broke at $i_{max} = 650$ A and that a cavity was formed in the middle of the rod, the 'central canal' which indicated that carbon was sublimated in the core of the rod due to high vapour pressure in the centre. In order to study these points the simple arrangement used in the present investigation is inadequate for reasons stated before.

EXPLANATION OF PLATE III

Cathode layer spectrum at 11 A, 220 v. (d. c.) of the

No. 1. Impure 'Kino-Homogen' carbon rods.

" 2. Purified carbon rods by the method (A).

" 3. Purified carbon rods by the method of resistance heating (method B).

(a) when the cathode is adjusted just below the edge of the circular diaphragm.

(b) when the cathode is adjusted just touching the edge of the diaphragm.

In the photograph attached the cathode layer spectrum of the carbon rods is found to be inverted which is not actually the case in the original negative plate. In each plate the iron spectrum is shifted due to the movement of the plate holder. Lines of the elements which show the " Glimmschicht " or cathode layer effect are wedge-shaped with maximum intensity at the base of the cathode layer. For boron the effect is scarcely apparent. The two doublet lines of B (2497.72, 2496.80) approach equal intensity over the entire height of the spectrum.

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